PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C12G 3/08

A1

(11) International Publication Number: WO 92/08783

(43) International Publication Date: 29 May 1992 (29.05.92)

(21) International Application Number: PCT/EP91/02120

(22) International Filing Date: 8 November 1991 (08.11.91)

(30) Priority data:
9024668.7 13 November 1990 (13.11.90) GB

(71) Applicants *(for all designated States except US)*: DOW DANMARK A/S [DK/DK]; Stavangervej 10, P.O. Box 149, DK-4900 Nakskov (DK). DOW DEUTSCHLAND INC. [DE/DE]; Industriestrasse 1, Postfach 20, D-7587 Rheinmunster 2 (DE).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)* : NIELSEN, Cark-Erik [DK/DK]; Skalkenaesvej 4, DK-4900 Nakskov (DK). THOMSEN, Mette, Moeller [DK/DK]; Noerrevold 3, St., DK-4900 Nakskov (DK). HEYBACH, Klaus [DE/DE]; Kirchbachstrasse 9, D-4330 Muehlheim 1 (DE).

(74) Agent: RAYNOR, John; W.H. Beck, Greener & Co., 7 Stone Buildings, Lincoln's Inn, London WC2A 3SZ (GB).

(81) Designated States: AT, AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CI (OAPI patent), CM (OAPI patent), CS, DE, DE (European patent), DK, DK (European patent), ES, ES (European patent), FI, FR (European patent), GA (OAPI patent), GB, GB (European patent), GN (OAPI patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC, MG, ML (OAPI patent), MN, MR (OAPI patent), MW, NL, NL (European patent), NO, PL, RO, SD, SE, SE (European patent), SN (OAPI patent), SU+,TD (OAPI patent), TG (OAPI patent), US.

Published
With international search report.

(54) Title: MEMBRANE PROCESS FOR THE DEALCOHOLIZATION OF NATURALLY FERMENTED BEVERAGES

(57) Abstract

Dealcoholization of a naturally fermented beverage comprising: A) optionally, contacting the beverage with a microfiltration membrane, to obtain a permeate and a retentate with, respectively, lower and higher concentrations of high molecular weight turbidity causing compounds; B) optionally, contacting beverage or the microfiltration permeate with a nanofiltration membrane, to obtain a permeate and a retentate with, respectively, lower and higher concentrations of aroma and flavor containing compounds, C) contacting the microfiltration permeate or the nanofiltration permeate with a reverse osmosis membrane, which selectively permeates ethanol and selectively retains aroma and flavor containing compounds, to obtain a permeate and a retentate with, respectively, higher and lower concentrations of ethanol, and lower and higher concentrations of aroma and flavor containing compounds.

+ See back of page

+ DESIGNATIONS OF "SU"

Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland			SN	Senegal
CI	Côte d'Ivoire	KR	Republic of Korea	SU+	Soviet Union
CM	Cameroon	LI	Liechtenstein	TD	Chad
CS	Czechoslovakia	LK	Sri Lanka	TG	Togo
DE	Germany	LU	Luxembourg	US	United States of America
DK	Denmark	MC	Monaco		

MEMBRANE PROCESS FOR THE DEALCOHOLIZATION OF NATURALLY FERMENTED BEVERAGES

This invention relates to two- and three step membrane processes for the removal of alcohol from naturally fermented beverage products. Additionally, this invention relates to systems useful in such processes.

Non-alcoholic and low alcoholic fermented beverages such as beers and wines have become of great interest lately because they offer traditional beer and wine flavor without certain unhealthy and socially objectionable side effects of alcohol. In particular, many people are becoming more concerned about their caloric intake, and are interested in food and beverages which have low caloric content. Therefore, alcoholic beverages which have lower calories have become more popular recently. As a major source of calories in beer and wine is found in the alcohol content, it is desirable to produce low alcohol or non-alcoholic beer and wine, and yet retain the flavor taste of such beer and wine.

Non-alcoholic and low alcoholic beer and wine have been marketed for a number of years, but the techniques applied in production of such beer and wine have produced off-flavors. For example, the alcohol can be distilled away, but in the process the beer or wine is cooked or at least denatured and much of the beer or wine flavor and aromatics are driven off or altered. Another method is to reduce alcohol content by dilution with water. This results in a thin taste which one can expect from a watered down beer or wine.

There are several methods disclosed in the art for removing or reducing alcohol in naturally fermented beverages which incorporate or use a membrane separation step. Bonneau US Patent 4,499,117 uses a three-step process comprising, first an nanofiltration step using an nanofiltration membrane with a molecular weight cutoff of about 10,000, followed by a single reverse osmosis step applied to the ultrafiltrate permeate using a Degremont brand reverse osmosis membrane which is prepared from aromatic polyamide hollow fibers which have a molecular weight cutoff of about 250. Thereafter, the permeate from the reverse osmosis step is subjected to a vacuum distillation step at about 0.15 atmospheres at a temperature of about 45°C. The product is the retentate of the three steps which is subsequently recombined. Note a significant number of the flavor and aroma compounds pass through the reverse osmosis membrane and are therefore subjected to the vacuum distillation step. At temperatures of about 45°C, such flavor and aroma compounds can be negatively affected, thereby deteriorating the flavor and aroma of the ultimate beverage produced. Goldstein US Patent

4,612,916 discloses the use of a reverse osmosis membrane to dealcoholize wine and malt beverages. In particular it is disclosed that such beverages can be prepared by a method which comprises subjecting a traditional beverage prepared by conventional fermentation to reverse osmosis using a thin film composite membrane which has a polyamide active barrier on a microporous polysulfone support. The membrane retains the volatiles and other flavor constituents of beer and allows 25 to about 30 % of the alcohol in the beverage to pass through the membrane. The Goldstein Patent compares thin film composite type membranes to a cellulose acetate type membranes and demonstrates that 99 % of the flavor and aroma materials are rejected by a thin film composite membrane, whereas only 16 % of such volatiles are rejected by a cellulose acetate asymetric membrane. Beaumont US Patent 4,441,678 discloses the use of nanofiltration on both grape juice and wine fermented therefrom. The grape juice and wine is passed through a membrane which has a molecular weight cutoff of 175 to 200 for the purpose of removing methyl anthranilate and other objectionable flavors in Labrusca-type wine grapes.

Keufner, UK Patent GB 2,133,418A published July 25, 1984, describes a process of concentrating beer and wine by passing it through a reverse osmosis semipermeable membrane, and later adding liquid to form a reconstituted beverage. The reconstituting water can be reverse osmosis treated water from which up to 99 % of the minerals have been removed. The membrane is a thin film composite on a polymeric support. The reverse osmosis system is operated at a temperature in the range

of about - 2 to about 40°C and at pressure of from about 100 - 110 psig in a non-oxidizing atmosphere provided by the presence of carbon dioxide. The reconstituting water is added after completion of the reverse osmosis process. Approximately 45 % of the alcohol and 75 % of the water was removed from the beer in the process. The resulting beer contained 2.3 % alcohol by weight. Of three samples produced, one had a slight burnt note in the aroma, and another sample was quite thin indicating not enough bodying ingredients remained after dilution. These can be characterized as light beers with low alcohol content.

Guinness Company's Belgian Patent 717,847 (Dec. 1968) employed reverse osmosis under a non-oxidating atmosphere to produce a concentrate for export which is reconstituted with locally produced alcohol. The preferred membrane is cellulose acetate as taught by US Patent 3,133,132. Also mentioned as membrane materials are polyvinyl acetate and polyacrylates. This patent teaches post-shipment reconstituting to the same volume with alcohol and water, or with water alone to get a non-alcoholic or almost entirely non-alcoholic beverage.

British Patent Specification No 1,447,505 relates to a process for the production of beer with a reduced, low or no alcohol content. This patent discloses a process for removing ethyl alcohol from beer using a membrane system which is operated in a batch-concentration type of system in which the beer which is being processes is either diluted with water prior to or subsequent to the process. However, this type of process possesses inherent disadvantages inasmuch as the

concentration of the other complex components which are present in the beer are altered, thereby leading to the probability that precipitates as well as other components which would foul the membrane can form. The precipitates and/or membrane foulants will therefore not only affect the taste of the beer,but will also reduce the productivity of the membrane system. In addition, the process which is described is operated at a relatively high pressure system.

Light US Patent 4,617,127 discloses low alcohol content beverages may be obtained by passing a high alcohol content beverage through a reverse osmosis system to form a permeate and a retentate. The permeate comprises mainly alcohol and water and is removed. A minor portion of the retentate is recovered as product, and a major portion is recycled back to the reverse osmosis system to admix with fresh beverage and added water. See also US Patent 4,717,482. Gnekow US Patent 4,888,189 discloses a simultaneous double reverse osmosis process for production of beverages, particularly wines, having a reduced level of alcohol from any traditionally fermented table wine as a feed-stock. All of the feed wine is subjected to reverse osmosis to remove alcohol and water as a permeate, with recycle of the concentrated retentate, while simultaneously or alternately a volume-balanced amount of reverse osmosis water is input back into the feed tank to maintain the initial level of the feedstock wine. The resulting finished wine has flavor, aroma and color solids concentration acceptable in good commercial practice. The process may be run batch-wise, or in a modified semi-continuous operation to produce non-

alcoholic wines (wines having residual alcohol content of less than 0.5 % volume percent alcohol), or wines having reduced alcohol content (less than 11-13 volume percent volume).

The known processes suffer from several problems. First, the use of an open reverse osmosis membrane, such as a cellulose acetate type, results in a significant loss of aroma compounds through the membranes. Alternatively, in those processes in which a relatively dense membrane, such as a thin film composite type membrane, is used the capacity is low, as the large molecular weight compounds tend to foul the membrane and reduce the efficiency of the membrane. Such high molecular weight compounds include proteins, betaglycanes, polysaccharides, and polyphenol complexes. This in essence lowers the liquid flux, and the alcohol permeability. As a result it requires an increasing demand for deionized water. Other of the disclosed processes expose the naturally fermented beverages to high temperatures or high pressures, either of which can damage the compounds which provide flavor and aroma, thereby significantly hurting the ultimate flavor and acceptability of the beverage.

What is needed is a process which economically removes ethanol from a natural fermented beverage while still retaining the aroma and flavor enhancing compounds. What is further needed is a process which does not result in damage by heat or pressure to aroma and flavor compounds. What is further needed is a process which does not result in degrading the

efficiency of the membranes used, for example by fouling the membranes and reducing the flux.

Another problem in the preparation of beers and wines is the presence of turbidity causing compounds. Generally these are very high molecular weight compounds which settle out the naturally fermented beverage after bottling. It has been discovered that compounds such as proteins and betaglycanes of high molecular weight create the turbidity and may detrementally affect the taste of the ultimate beverage. What is desired is a process for preparing low alcohol beverages which results in beverages which do not contain such turbidity causing compounds.

The invention herein meets the above-described needs. In one aspect the invention is a process for the dealcoholization of a naturally fermented beverage comprising:

A. optionally, contacting a microfiltration feed stream comprising a naturally fermented beverage with a microfiltration membrane, having a pore size of 0.1 to 1.0 μm, under conditions such that the feed stream is separated into a microfiltration permeate stream which has a lower concentration of high molecular weight turbidity causing compounds, and a microfiltration retentate stream which has a higher concentration of high molecular weight turbidity causing compounds as compared to the microfiltration feed stream;

B. optionally, contacting a nanofiltration feed stream comprising a naturally fermented beverage or

the microfiltration permeate stream with a nanofiltration membrane, having a molecular weight cutoff of from 100 to 10,000, under conditions such that the nanofiltration feed stream is separated into an nanofiltration permeate stream which has a lower concentration of aroma and flavor containing compounds, and an nanofiltration retentate stream which has a higher concentration of aroma and flavor containing compounds as compared to the nanofiltration feed stream;

C. contacting a reverse osmosis feed stream comprising the microfiltration permeate or the nanofiltration permeate with a reverse osmosis membrane, which selectively permeates ethanol and selectively retains aroma and flavor containing compounds under conditions, such that the reverse osmosis feed stream is separated into a reverse osmosis permeate stream which is higher in ethanol concentration and lower in aroma and flavor containing compounds, and a retentate stream which is lower in ethanol concentration and higher in aroma and flavor containing compounds, as compared to the reverse osmosis feed stream;

characterized in that, either or both of steps A. or B. must be performed, and if step B is performed the reverse osmosis retentate and the nanofiltration retentate are recombined subsequent to step C.

In another embodiment the invention is an apparatus for performing the above-described process. The process and apparatus claimed and described herein allow the preparation of naturally fermented beverages without removing or damaging aroma or flavor compounds.

Furthermore the process removes compounds which create turbidity and negatively affect the taste. Furthermore the process and apparatus provided economical means for achieving the above-described aims.

Briefly, Figure 1 demonstrates a process using a microfiltration step, a nanofiltration step, and a reverse osmosis step. The figure further describes recycling the retentate of the nanofiltration membrane and recycling retentate of the reverse osmosis membrane. Figure 2 describes a process which comprises a nanofiltration step and a reverse osmosis step in which the retentate from both steps are recycled. Figure 3 describes a process in which a microfiltration, and a reverse osmosis step are used wherein the retentate from the reverse osmosis step in recycled.

The following definitions are useful in understanding the invention described herein. Naturally fermented beverages as used herein refer to beverages prepared by fermenting a naturally occurring feed stock. Included in such naturally fermented beverages are wine, beer, ale, stout, perry's and the like.

Molecular weight cutoff is an expression of the retention characteristics of a membrane in terms of molecules of known sizes. The retention or molecular weight cutoff is the molecular weight at which at least 90 % of sperical uncharged molecules of that same molecular weight are retained by the porous membrane,

whereas less than 50 % of such molecules of significantly lower molecular weight are not retained. Feed as herein refers to the original material fed to a membrane, and may optionally include a recycled concentrate, or a mixture thereof. A membrane separation process results in a production of two liquid fractions, the permeate fraction which passes through the membrane, and the retentate fraction which does not pass through the membrane. Permeate refers to a liquid and materials dissolved, suspended, and the like in such liquid, which passes through the membrane. Retentate refers to the liquid, including materials dissolved, suspended and the like in such liquid, which does not pass through the membrane. Note that aroma and flavor compounds as used herein refer to certain organic compounds which are contained in the naturally fermented beverage and which give the naturally fermented beverage its aroma and flavor, included for example in such compounds are propanol, higher aldehydes, acetates and ethers. Included in such compounds are n-propanol, ethylacetate, and isoamyl alcohol.

As used herein, turbidity producing compounds refer to very high molecular weight proteins and betaglycanes which precipitate from the naturally fermented beverage upon setting. Generally such compounds have molecular weights above 200,000.

There are several modes in which the invention claimed herein can be performed. The reverse osmosis step is required in all of the modes. Prior to the

reverse osmosis step, either the microfiltration step, or the nanofiltration step must be performed. In certain circumstances it may be desirable to perform both steps. The choice of which mode to be used is to determined by economics and the nature of the naturally fermented beverage to be treated by the process. One skilled in the art would be able to determine which mode would be best suited economically and technically for the particular feed used. If the nanofiltration step is used, then the retentate from the nanofiltration step is combined with the retentate from the reverse osmosis step to form a reconstituted beverage which contains substantially all of the aroma and flavor containing compounds with a significantly lower concentration of ethanol.

In one embodiment, the process of the invention comprises first feeding the naturally fermented beverage to a microfiltration membrane, having a pore size of 0.1 to 1.0 microns, under conditions such that the retentate contains a higher concentration of the turbidity causing compounds, for instance high molecular weight proteins and betaglycanes. The permeate contains the naturally fermented beverage with a significantly lower concentration of turbidity causing compounds as compared to the feed composition. Thereafter the microfiltration permeate is fed to a nanofiltration membrane having a molecular weight cutoff of from 100 to 10,000, under conditions such that the permeate contains a high concentration of water and ethanol and a retentate contains a high concentration of aroma and flavor containing compounds. Thereafter the permeate stream from the nanofiltration is fed to the reverse osmosis

membrane under conditions such that ethanol selectively permeates through the reverse osmosis membrane, and retentate has a significantly lower ethanol concentration. Thereafter, the naturally fermented beverage, without ethanol or with significantly lower concentration of ethanol, is reconstituted by combining the retentate from the reverse osmosis process with the retentate from the nanofiltration process, and optionally water.

In another embodiment of the invention, the naturally fermented beverage is fed to a microfiltration membrane as described hereinbefore to form a retentate of with a higher concentration high molecular weight turbidity causing compounds, and a permeate of the naturally fermented beverage with a significantly lower concentration of the turbidity causing compounds as compared to the feed. Permeate from the microfiltration step, is fed to the reverse osmosis membrane, under condition such that the ethanol selectively permeates through the membrane, such that the retentate comprises the naturally fermented beverage with a lower concentration of ethanol than the feed to the reverse osmosis membrane. Optionally, water may be added to the reverse osmosis retentate so as to replace the volume of the liquid which permeates through the reverse osmosis membrane.

In yet another embodiment of the invention, the process involves feeding the naturally fermented beverage to a nanofiltration membrane under conditions

such that the permeate comprises a stream with higher ethanol concentration than the retentate, and the retentate stream contains a higher concentration of aroma and flavor containing compound as compared to the feed stream. Thereafter the permeate from the nanofiltration step is fed to the reverse osmosis step under conditions such that the permeate through the reverse osmosis membrane has a higher concentration of ethanol than the feed stream, and the retentate from the reverse osmosis process contains a significantly lower concentration of ethanol as compared to the feed stream. Thereafter, the retentate from the nanofiltration membrane, and the retentate from the reverse osmosis process are recombined, optionally with water, to prepare a reconstituted naturally fermented beverage which contains substantially all of the aroma and flavor containing compounds, with a significantly lower concentration of an ethanol therein.

The microfiltration step is designed to remove high molecular turbidity causing compound, which do not add to or which take away from, the flavor and aroma of naturally fermented beverages. Microfiltration as used herein refers to a process whereby high molecular weight compounds are removed by passing the naturally fermented beverage through a membrane which functions as a filter for high molecular weight compounds. The term microfiltration, as used in the membranes field has taken on different meanings to different skilled artisans. In general, it relates to the separation of high molecular weight materials from a liquid stream by passing the streams through a membrane of a certain pore size which is relatively large. The difference in

definition between skilled artisans relates to the lower treshhold of pore size of microfiltration. As used herein microfiltration is used to refer to a membrane having a pore size of from 0.1 to 1.0 μm. Membranes useful for this step are well-known in the art. Such membranes generally are homogeneous or asymetric porous membranes prepared from a polymer which is inert with respect to the naturally fermented beverage to be processed, and which has sufficient chemical resistance and morphological strength to withstand the conditions under which the process is performed. Such membranes can be prepared from polyolefins, such as polyethylene or polypropylene, polycarbonates, halogenated polycarbonates, fluorinated polyolefins, such as polyvinylidene flouride, polysulfones and polyether sulfones. Preferred materials are polysulfones, polyethersulfones, and florinated polyolefins. More preferred are the membranes prepared from polyvinylidene fluoride and polysulfone. Generally,for membranes having a pore size at the upper end of the range disclosed hereinbefore are homogeneous membranes. Whereas at the lower end of such range asymetric membranes are used.

In this step the feed to the membrane is a naturally fermented beverage, that is wine, beer, ale, stout and the like. The feed is separated into two streams, the retentate stream containing a higher concentraction of the high molecular weight turbidity compounds such as proteins and betaglycanes, as compared to the feed. The permeate contains the naturally fermented beverage with a lower concentration of such higher molecular weight compounds, as compared to the

feed, which further comprises the water, ethanol, aroma and flavor compounds. For the purpose of preparing a naturally fermented beverage of low alcohol content the retentate may be of no other use. The permeate is used for feeding the down stream processes.

The feed is contacted with the membrane at a pressure sufficient to drive the permeate across and through the membrane. The applied pressure should be sufficient to provide a sufficient driving force to drive the permeate across and through the membrane, and also to retain the necessary volatile components, such as carbon dioxide, in the naturally fermented beverage. On the other hand the applied pressure should not be so high as to cause unnecessary fouling of the membrane. If pressure is to high, molecular weight compounds are driven against the membrane and may remain there resulting in a lower flux across the membrane and an inefficient process. Preferably, the applied pressure is between about 2 and 3.5 bar (0.2 and 0.35 mPa.s). More preferably the applied pressure is between about 3 and 3.5 bar (0.3 to 0.35 mPa.s). In order for a membrane process to work properly there must be a sufficient driving force to drive the permeate across the membrane, generally this is a difference in pressure across the membrane, commonly referred to as transmembrane pressure. Preferably, the transmembrane pressure is greater than 0.5 bar (0.05 mPa.s). When the natural fermented beverage is a beverage that contains carbon dioxide, such as beer, 1.75 bar (.175 mPa.s) is the minimum pressure necessary to retain the carbon dioxide in the beverage. Preferably the transmembrane pressure is 3.0 bar (0.3 mPa.s) or less. The temperature used in

the process can have significant effect on the ultimate taste and aroma of the beverage. If too low a temperature is used the components may freeze, or important flavor and aroma containing compounds may precipitate out of the beverage. If too high a temperature is used, damage can occur to the flavor and aroma containing compounds. Preferred temperatures are between about 2 and 10°C, most preferred temperatures between about 2 and 8°C. The flow rates across the membrane are important, with respect to the economic aspects of the process. Preferably flow rates are from 100 to 3,000 l per m^2/h are preferred. Generally in such a process the flow rates of permeate through the membrane start at a high level and level off after a period of time, for example 1 to 2 hours. Preferably, after 2 hours the membranes exhibit a flow rate of between about 100 and 500 l/m^2/h, more preferably from 200 to 250 l/m^2/h.

Such membranes are preferably contained in membrane modules. The configuration of such modules are well-known in the art. Preferably, spiral wound or plate and frame devices are used.

The second step is a nanofiltration step. The nanofiltration step is designed to retain the medium molecular weight aroma and flavor compounds from the process stream, such that the medium molecular weight aroma and flavor containing compounds do not foul the reverse osmosis membrane in the reverse osmosis step. Preventing fouling of reverse osmosis membranes results

in a higher flux in the reverse osmosis membrane, and a more economical reverse osmosis step. Whether or not, the nanofiltration step is used is dependent on the balance between the processing costs added as a result to fouling of the reverse osmosis membrane versus the capital cost and the extra processing cost as a result of the using of the nanofiltration step. A further advantage of the nanofiltration step is that such step reduces the osmotic pressure which must be overcome in the reverse osmosis step, thereby reducing the amount of pressure which must be applied to the feed in such step.

The nanofiltration membranes refer herein to membranes having molecular weight cutoff of from 100 to 10,000, and most preferably from 100 and 1,000. Generally the nanofiltration membrane is an asymetric membrane with pores having the molecular weight cutoffs described hereinbefore. Such membranes are well-known to those skilled in the art, and may be prepared from cellulose acetates, regenerated cellulose acetate, aliphatic polyamides, aromatic polyamides, and polyvinyl alcohol. Preferred membranes are prepared from cellulose acetate, aliphatic polyamides regenerated cellulose acetate, polyvinyl alcohol. More preferred membranes are prepared from cellulose acetate or aliphatic polyamide. Such membranes may also be thin film composites comprising a thin film of a discriminating layer on a porous asymetric support. Such porous asymetric supports may be prepared from polyolefins, halogenated polyolefins, e.g. fluorenated polyolefins, polycarbonates, polysulfones or polyether sulfones. Preferred support materials are polysulfone, polyether sulfone and fluorinated polyolefins, such as

polyvinylidene fluoride. The discriminating layer may comprise a polyurethane, hydroxyalkyl cellulose, polyvinyl alcohol, or polyamide thin film deposited on the support. In one preferred embodiment the thin film is the interfacial reaction product of a di or tri functional aromatic acid halide, or mixture thereof, with a di or trifunctional polyamine such as piperazine or substituted piperazine. Examples of such membranes are disclosed in Cadotte US Patent 4,259,183, Fibiger US Patent 4,769,148, Kamiyama US Patent 4,619,767 and Uemura US Patent 4,595,139, all incorporated herein by reference. Nanofiltration membranes are usually disposed in a membrane module. Several configurations of membrane modules are well-known to the skilled artisan, for example plate and frame, spiral wound, hollow tube, and hollow fiber. The choice of membrane module used is dependent upon how the process is performed. One skilled in the art can readily determine which of the membrane configuration best suits the needs of the process. Preferably, the modules are spiral wound, or plate and frame type.

The feed to the nanofiltration step is either the naturally fermented beverage, or the permeate from the microfiltration step. The feed stream is separated into a retentate stream which has a higher concentration of aroma and flavor containing compounds as compared to the feed stream, and a lower ethanol concentration as compared to the feed stream. The permeate is a stream which is higher in ethanol concentration and lower in concentration of the aroma and flavor containing compounds as compared to the feed stream.

As membrane processes rarely result in a complete separation it may be desirable to recycle the retentate back to be fed to the nanofiltration membrane, or to further treat the retentate by feeding it to additional nanofiltration membranes so as to further reduce the ethanol content of such streams. Note that the feed to the nanofiltration membrane may comprise, in addition to the permeate from the microfiltration step or the naturally fermented beverage, retentate which has been recycled from a previous nanofiltration step, or, optionally make-up water.

Preferably the feed pressure to the nanofiltration membrane is sufficient to create a sufficient driving force to drive the permeate across and through the membrane. If the feed pressure is too low, there will not be sufficient driving force to force the permeate through the membrane, if the feed pressure is too high unnecessary fouling of the membrane results, thereby reducing the flow through the membrane and resulting in a less economic process. Preferred lower feed pressures are 30 bar (3.0 mPa.s). A preferred upper feed pressure is 60 bar (6.0 mPa.s). A more preferred upper feed pressure is 40 bar (4.0 mPa.s). Generally the transmembrane pressure must be sufficient to provide a sufficient driving force. As the transmembrane pressure is a function of the applied pressure, if the transmembrane pressure is too high significant fouling of the membrane will result. Preferably the lower limit on transmembrane pressure is 28 bar (2.8 mPa.s). Preferably to upper limit on transmembrane pressure is 58 bar (5.8 mPa.s),

and most preferably 38 bar (3.8 mPa.s). The flow rate across the membrane should be sufficient such that the process becomes economical to run. If the flow rate is too low the process becomes unaffordable, insufficient separation results, and membrane fouling may result. If the flow rate is too high, the energy consumption is too high and the process becomes uneconomical. Preferably the lower limit on flow rate is 50 $l/m^2/h$, more preferably 200 $l/m^2/h$. Preferably the upper limit on the flow rate is 300 $l/m^2/h$, with 250 $l/m^2/h$ being more preferred. The temperature at which this process may be performed is the same as described with respect to the microfiltration step.

Because a membrane separation is rarely a precise separation, it may be desirable to further concentrate the nanofiltration retentate stream by either recycling the retentate as feed to the nanofiltration process, or passing it to one or more other nanofiltration membranes arranged in series. In the embodiment wherein a series of nanofiltration membranes are used, the retentate would be fed to one or more other nanofiltration membranes, the number of membranes being chosen to result in the desired ethanol concentration level in the retentate. When the retentate is recycled, it may be recycled directly to a feed line, or recycled to a holding vessel. In a preferred embodiment of performing the nanofiltration process, the feed to the nanofiltration membrane is placed into a holding vessel and thereafter the material from the holding vessel is fed directly to the nanofiltration membrane. In the recycle scheme, the retentate from the nanofiltration step is returned to the holding vessel. The material in the holding vessel

may be passed through the nanofiltration membrane several times in order to result in a sufficient concentration of the feed to the nanofiltration membrane, and a sufficient lowering of the ethanol level. The preferred concentration degree is between about 1.5 and 10, more preferably between about 2 and 3. Optionally, water may be added during the concentration of the material of the holding tank, generally one skilled in the art would recognize how much water to add. Preferably water is added to replace the volume of permeate through the nanofiltration membrane.

A third step is a reverse osmosis step, wherein ethanol is separated from the remainder of the naturally fermented beverage. In particular the membrane used should be chosen to allow the passage of ethanol through the membrane in the permeate stream, and prevent significant permeation of aroma and flavor compounds through the membrane. Preferably, the membrane has the molecular weight cutoff of between about 40 and 100. More preferably the membrane has a cutoff of between about 40 and 50. Generally above a molecular weight of 100, aroma and flavor containing compounds may significantly permeate through the membrane. Below about 40 ethanol will not significantly permeate through the membrane. Any reverse osmosis membrane known to those skilled in the art which has the above-described permeability characteristics may be used. Such reverse osmosis membranes are well known to those skilled in the art. Preferred membranes are thin film composite membranes, which comprise an asymetric support membrane with a thin film of polymer deposited thereon, wherein the thin film of polymer controls the permeation

characteristics of the membrane. More preferably, such thin film composite membranes have a polyamide discriminating layer prepared from piperazine, or substituted piperazine, reacted with a polyvalent acyl halide, more preferably such thin film discriminating layer is prepared from piperazine, or substitute of piperazine and trimesoyl chloride and optionally, a difunctional acyl chloride. Such membranes are further described in US Patent 4,259,183 which is incorporated herein by reference.

The feed to the reverse osmosis membrane depends upon which of the previous membrane separation steps were previously performed. In general, the feed is the permeate from either the microfiltration membrane, or the nanofiltration membrane. In that embodiment where both processes are used then the feed is the permeate from the microfiltration which is further permeated through the nanofiltration membrane. Furthermore the feed may comprise a recycled retentate from the reverse osmosis membrane, and further make-up water which is desirable to keep the process properly running. In general, the separation results in a stream of retentate which has a higher concentration of flavor and aroma compounds which pass through the previous processing steps than in the feed. Such a retentate has a lower ethanol concentration than the feed. The permeate is primarily water and ethanol wherein the ethanol concentration is higher than the feed, with little if any, aroma and flavor containing compounds.

The feed pressure required is significantly lower when there is a lower risk of fouling of the membrane due to the presence of higher molecular weight compounds. If the feed pressure is too low, then insufficient driving force is provided to overcome the osmotic pressure of the permeate side and insignificant permeate is produced. If the pressure is too high membrane fouling occurs, or risk of damage to the membrane is present. Preferably the lower feed or applied pressure is 20 bar or greater (2.0 mPa.s), more preferably 25 bar or greater. Preferably, the feed pressure is 60 bar (6.0 mPa.s) or less, and more preferably 30 bar (3.0 mPa.s) or less. The temperature at which this process may be performed is from 2-30°C, preferably 2-10°C.

If the flow rate through the membrane is too low the process is uneconomical, the flow rate is too high the separation is compromised. Preferably the flow rate is 10 $l/m^2/h$ or greater, more preferably 20 $l/m^2/h$ or greater. Preferably the flow rate is 50 $l/m^2/h$ or less, more preferably 40 $l/m^2/h$ or less. In general, contacting the feed with the reverse osmosis membrane module once may not be sufficient to remove the desired amount of ethanol, thus the retentate may have a higher ethanol concentration than desired. In order to achieve the desired ethanol level in the retentate, the retentate may be passed through a series of reverse osmosis membranes, or the retentate may be recycled and fed to the same reverse osmosis membrane. In one embodiment the retentate may be recycled to the feed line and fed right into the process, in another embodiment, the permeate from the microfiltration or

nanofiltration process may be fed to a holding vessel, and the retentate from the reverse osmosis process may be fed to the same vessel. Optionally make-up water may be added to this vessel. From this holding vessel is taken the feed to the reverse osmosis membrane. In a preferred embodiment, the retentate from the reverse osmosis membrane is continually recycled to the holding vessel until the desired level of ethanol of the mixture contained in the holding vessel is achieved. In a preferred embodiment water is added to the tank in volumes substantially equal to the volume of permeate through the reverse osmosis membrane. Generally, the number of reduction degrees depends upon the desired product. For example in Germany, low alcohol beer is defined as having 2 % by volume or less alcohol in it, whereas no alcohol beer is defined by having 0.5 % by volume of alcohol contained therein. In the United Kingdom low alcohol beer is 1.2 % by volume, whereas alcohol free is 0.5 % by volume alcohol. Therefore the desired level of ethanol in the final product is different, depending upon the classification of the fermented beverage and the country into which it is being marketed. Preferably, the reduction degrees used are between about 2 and 15, most preferably between about 2 and 8.

In one embodiment, it is desirable to concentrate the reverse osmosis retentate in the holding tank to a certain degree before adding make up water. In such embodiment, the amount of water added to the holding vessel is lower than the amount of permeate through the reverse osmosis during concentration. In such embodiment less make up water is required. Preferably the make up water is deionized. The water can

be deionized by known processes, for example, diafiltration. As deionization of water is costly, minimization of its use is desirable. Once make up water is added to a step, it may be continually added. Two preferred modes of water addition may be used. In one embodiment wated is added such that flow rates across the membrane remain constant. In another embodiment, water is added to maintain constant volume in the holding tank.

In order to reconstitute the beverage, the retentate from the nanofiltration process and the reverse osmosis process are recombined. Such recombination can take place in a batch tank, or may take place in a plug-flow type mixing device. The idea is to return the natural aromas and flavors to the processed naturally fermented beverage.

The preferred feed to the process and apparatus of this invention is beer.

In another embodiment the invention comprises an apparatus adapted for performing the above-described process. This apparatus comprises:

A. optionally, one or more microfiltration membrane modules, wherein the membrane has a pore size of from 0.1 to 1.0 μm;

B. optionally, a means for introducing a naturally fermented beverage to the microfiltration membrane module;

C. optionally, a means for removing a microfiltration retentate from the vicinity of the microfiltration membrane module;

D. optionally, a means for removing a microfiltration permeate from the vicinity of the microfiltration membrane module;

E. optionally, one or more nanofiltration membrane modules, wherein the membrane has a molecular weight cutoff of from 100 to 10,000;

F. optionally, a means for introducing a naturally fermented beverage or microfiltration permeate to the nanofiltration membrane module;

G. optionally, a means for removing a nanofiltration retentate from the vicinity of the nanofiltration membrane module;

H. optionally, a means for removing a nanofiltration permeate from the vicinity of the nanofiltration membrane module;

I. one or more reverse osmosis membrane modules containing a membrane which is capable of selectively permeating ethanol and selectively retaining flavor and aroma compounds of naturally fermented beverages;

J. a means for introducing microfiltration permeate or nanofiltration permeate to the reverse osmosis membrane module;

K. a means for removing a reverse osmosis retentate from the vicinity of the reverse osmosis membrane module;

L. a means for removing a reverse osmosis permeate from the vicinity of the reverse osmosis membrane module;

characterized in that all of elements A B C and D, if present, are present together, all of elements E F G and H, if present, are present together, and that either the set of elements A B C and D, the set of elements E F G and H, or both sets of elements must be present;

further characterized in that where elements E F G and H are present the element M shall be included which comprises,

M. a means for combining the nanofiltration retentate and the reverse osmosis retentate.

It should be noted that elements A, B, C and D, as described hereinbefore, comprise an integral unit. In particular, B the means for introducing the naturally fermented beverage to the microfiltration module is only necessary if the microfiltration membrane module is present, whereas the same is true for C and D which relate to removal of the retentate and permeate from the microfiltration membrane module. Additionally element E, F, G and H are also integrally related. Element F relates to introducing the feed stream to the nanofiltration membrane module, and elements F and G relate to removing the permeate retentate, respectively, from such nanofiltration membrane module. As described

hereinbefore with respect to the process, either a microfiltration or a nanofiltration membrane module is required, therefore either, or both, of the two sets of elements described hereinbefore must be present. Furthermore, if the nanofiltration membrane and its integrated feed and removal means are present, than the means for recombining the nanofiltration retentate with the reverse osmosis retentate is required, element M.

The microfiltration module, contains a membrane which has a pore size of 0.1 to 1.0. This membrane module may be any microfiltration membrane module known to those skilled in the art. It may be in the configuration of a plate and frame, spiral wound, or hollow tube. Preferably it is a spiral wound or plate-and-frame membrane module. Such modules are well known to those skilled in the art and readily available on the market. The means for introducing the naturally fermented beverage to the microfiltration module generally is a conduit which further contains necessary valving, and preferably contains a pump which is sufficient to provide the feed at a pressure which provides the necessary feed pressures to allow for permeation through the microfiltration membrane. The means for removing the microfiltration retentate from the vicinity of the microfiltration module is generally an orifice in the membrane module and a conduit for removing the retentate from the module. The means for removing the microfiltration permeate, is generally one or more orifices in the membrane module which are connected with a conduit for removing the permeate from the vicinity of the microfiltration membrane module.

The nanofiltration membrane module, contains a nanofiltration membrane as described hereinbefore. The module may be of any configuration well-known to those skilled in the art including hollow fiber, hollow tube, spiral wound and plate-and-frame. Preferably it is a spiral wound or plate-and-frame module. Such membrane modules are well-known to those skilled in the art and readily available. The means for introducing the naturally fermented beverage or microfiltration permeate to the nanofiltration module is a feed line or conduit, which preferably has incorporated therein or connected thereto, a pump which functions to pressurize feed to the nanofiltration membrane module to a sufficient level which allows for economic permeation of the permeate across and through the nanofiltration membrane.

The means for removing the nanofiltration retentate from the vicinity of the nanofiltration membrane is generally one or more orifices in the nanofiltration module connected to conduits which remove the retentate from vicinity nanofiltration module. The means for removing the nanofiltration permeate generally relates to one or more orifices in the module, along with conduits designed for removing the nanofiltration permeate from the vicinity of the nanofiltration membrane module.

The reverse osmosis membrane is described hereinbefore, and the reverse osmosis membrane modules are modules which contain such membranes. Such modules

are well-known to those skilled in the art and may be of hollow fiber, hollow tube, spiral wound, or plate-and-frame configuration. Preferred configurations are the spiral wound and plate-and-frame. Such membrane modules are well-known to those skilled in the art and readily available. The means for introducing the feed to the reverse osmosis membrane module is generally a conduit or pipe which preferably contains a pump which pressurizes the feed to a sufficient level to allow the permeate to pass across and through the reverse osmosis membrane. The means for removing the reverse osmosis retentate from the reverse osmosis membrane is generally a one or more orifices in the reverse osmosis membrane module along with a conduit for removing such retentate. The means for removing the reverse osmosis permeate from the vicinity of the reverse osmosis membrane module generally involves orifices in the membrane and module conduit for removing the permeate.

The means for combining the nanofiltration retentate and the reverse osmosis retentate involves either a holding vessel, mixing tank or some kind of plug flow type mixing vessel in which the retentate or of the nanofiltration membrane along with the retentate of the reverse osmosis material are contacted and mixed.

In a preferred embodiment the apparatus further comprises a holding vessel which is adapted for receiving the nanofiltration permeate from the means for removing the nanofiltration permeate from the vicinity of the nanofiltration membrane module or the microfiltration

permeate from the means for removing a microfiltration permeate from the vicinity of the microfiltration membrane module. In this embodiment, the apparatus further comprises a means for transporting the contents of the holding vessel to the reverse osmosis membrane module, a means for recycling the reverse osmosis retentate to the holding vessel; and a means for adding water to the holding vessel to make up for some or all of the volume of reverse osmosis permeate. In those embodiments where a holding vessel is used to feed the reverse osmosis membrane module, the permeate from the microfiltration membrane module, or the nanofiltration membrane module is introduced to this holding vessel via the means for removing the permeate from the microfiltration membrane module, or from the nanofiltration membrane module. This holding vessel is connected to the reverse osmosis membrane module via the means for transporting the contents of the holding vessel to the reverse osmosis membrane module. This means is connected to a means for introducing feed to the reverse osmosis membrane. In fact, the means for transporting contents of the holding vessel to the reverse osmosis membrane is intimately connected with the means for introducing feed to the reverse osmosis membrane and the two means comprise generally connected conduits which preferably also has integrated therein an appropriate pump. The means for recycling the reverse osmosis retentate to the holding vessel is connected to the means for removing the retentate from the reverse osmosis membrane module. This may comprise a set of intimately connected conduits, said conduits being connected to the orifices in the reverse osmosis membrane module designed for removing retentate. The means for introducing make-up water to the holding vessel comprises a source of make-up water and conduits

designed to deliver make-up water to the holding vessel. The conduits for delivering the make-up water, may deliver the make-up water to the means for recycling the retentate, or may deliver the make-up water directly to the holding vessel.

In another embodiment the apparatus further comprises a holding vessel adapted to hold the material to be fed to the nanofiltration membrane which comprises a naturally fermented beverage or the permeate from the microfiltration membrane module. Such apparatus may further comprise a means of recycling the nanofiltration membrane retentate to said holding vessel. Such apparatus would further comprise a means for transporting the contents from the holding vessel to the nanofiltration membrane module and also a means for transporting the concentrated retentate contained in the holding vessel to a means for combining the nanofiltration retentate and the reverse osmosis retentate. In such embodiment the feed to the nanofiltration membrane is placed into a holding vessel. In the embodiment where a microfiltration membrane module is used, then the means for removing permeate from the microfiltration module would be connected directly to the holding vessel so as to conduct the permeate from the microfiltration membrane module to the holding vessel. The means for recycling the nanofiltration retentate to the holding vessel, is intimately connected to the means for removing the nanofiltration retentate from the nanofiltration membrane module. Such means comprise an intimately connected series of conduits designed to direct the nanofiltration retentate from the nanofiltration module

to holding vessel. Furthermore the means for transporting the contents of the holding vessel to the nanofiltration membrane module is intimately connected with the means for introducing feed to the nanofiltration membrane module, and such means generally comprise a series of conduits which preferably further comprise a pump for pressurizing the feed to the nanofiltration membrane module. In such embodiment, the apparatus further comprises a means for transporting concentrated retentate retained in the holding vessel to the means for combining the nanofiltration membrane retentate and reverse osmosis retentate. Such means is preferably a conduit which connects the holding vessel with the means used to combine the two retentate streams.

In one embodiment the means for removing the microfiltration permeate from the vicinity of the microfiltration module, is intimately connected with the means for introducing feed to the nanofiltration membrane module. Such means would generally comprise a series of conduits, preferably further comprising a pump, designed to conduct microfiltration permeate to the nanofiltration membrane module. In another embodiment, the means for removing the microfiltration permeate from the vicinity of the microfiltration membrane module would be connected with the means for introducing the microfiltration permeate, or feed, to the reverse osmosis membrane module. Such combined means would generally be a series of conduits, preferably containing a pressurization pump, adapted for transporting the microfiltration permeate to the reverse osmosis membrane module. In yet another embodiment, the means for

removing the nanofiltration membrane permeate from the vicinity of the nanofiltration module, would be connected with the means for introducing feed to the reverse osmosis membrane. These combined means are generally a series of conduits or pipes, preferably containing a pressurization pump, designed for delivering feed to the reverse osmosis membrane module.

The apparatus as described herein is further illustrated provided by the figures. Figure 1 discloses an apparatus for dealcoholization of a naturally fermented beverage which contains a microfiltration membrane module, an nanofiltration membrane module and a reverse osmosis membrane module. With reference to Figure 1, a conduit, 11, containing a pump, 12, feeds naturally fermented beverage to a microfiltration membrane module, 13, which contains a microfiltration membrane, 14. The naturally fermented beverage is separated into a retentate stream, generally containing high molecular weight proteins and betaglycanes, which is removed by a conduit, 15. The permeate through the microfiltration membrane, 14, is the naturally fermented beverage with a lower concentration of proteins and betaglycanes than the feed. The permeate is removed from the microfiltration membrane module, 13, via a conduit, 16, and passed through a valve, 17, which controls the flow of liquid to a first holding vessel, 18. The liquid is introduced to the holding vessel, 18, via conduit 19. The liquid from the first holding vessel is removed via a conduit, 20, and flow from the first holding vessel, 18, is controlled by a valve, 21. The material removed from the first holding vessel, 18, is thereafter introduced via a conduit, 22, to a nanofiltration

membrane module, 23, containing a nanofiltration membrane, 24. Integrated into the conduit, 22, is a pump, 25, adapted for pressurizing the feed to the nanofiltration membrane module 23. The retentate from the nanofiltration membrane module, 23, is recycled via a conduit, 26. Valve, 17, is adjusted to allow the nanofiltration retentate removed via the conduit, 26, to be recycled to the first holding vessel, 18. The permeate from the nanofiltration membrane module, 23, is removed via a conduit, 27, which passes through a valve, 28, which controls flow to a second holding vessel, 29. The nanofiltration permeate is introduced to the second holding vessel, 29, via a conduit 30. The contents of the second holding vessel, 29, may be removed by a conduit, 31. The flow of material from the second holding vessel, 29, is controlled by a valve, 32. A conduit, 33, conducts liquid removed from the second holding vessel, 29, to reverse osmosis membrane module, 34, containing a reverse osmosis membrane 35. Conduit 37 removes the reverse osmosis retentate from the vicinity from the reverse osmosis membrane module, 34, and returns it to holding tank, 29, through a valve, 28. A conduit, 38, removes the reverse osmosis permeate from the reverse osmosis membrane module, 34. Once the nanofiltration retentate has been concentrated to the desired degree, the concentrated nanofiltration retentate is transported via a line, 20, through a valve, 21, to a line, 39, which transports the nanofiltration concentrate to a mixing tank, 40. The reverse osmosis concentrate, once the desired ethanol concentration level is achieved, is removed from the holding vessel, 29, via a conduit, 31, and directed via a valve, 32, to a conduit, 41, which directs the reverse osmosis concentrate to a mixing tank, 40, wherein the nanofiltration and reverse osmosis

retentates are mixed and the dealcoholized naturally fermented beverage is reconstituted. A source of make-up water, 42, is connected to the second holding tank, 29, by a conduit 43. Product is removed from the mixing tank via conduit 44.

Figure 2 relates to an apparatus comprising a nanofiltration membrane module and a reverse osmosis membrane module. Naturally fermented beverage is introduced via a conduit, 19, to a first holding vessel, 18, through a valve, 17. The naturally fermented beverage is removed from the first holding vessel, 18, via a conduit, 20, the flow of liquid from the first holding vessel, 18, is controlled by a valve, 21. A conduit, 22, conducts the naturally fermented beverage to a nanofiltration membrane module, 23, containing a nanofiltration membrane, 24. Integrated into conduit 22, is a pump 25, adapted for pressurizing the naturally fermented beverage to an appropriate pressure to facilitate transport across the nanofiltration membrane 24. The retentate is removed via a conduit, 26, from the nanofiltration membrane module, 23, and recycled to the first holding vessel, 18, through a valve, 17. The permeate from the nanofiltration module, 23, is conducted via a conduit, 27, through a value, 28, to a second holding vessel, 29. The nanofiltration permeate is introduced to a second holding vessel, 29, via a conduit, 30. The nanofiltration permeate is removed via a conduit, 31, and passed through a valve, 32, adapted for controlling the flow of liquid from the second holding vessel, 29. A conduit, 33, passes the material from the second holding vessel, 29, to a reverse osmosis membrane module, 34, having a reverse osmosis membrane,

35. Such conduit, 33, has integrated therein a pump, 36, adapted for pressurizing the feed to the reverse osmosis membrane module, 34. The permeate from the reverse osmosis membrane module, 34, is removed via a conduit, 38. The retentate from the reverse osmosis membrane module, 34, is removed from the vicinity from the reverse osmosis membrane module, 34, via a conduit, 37, which is connected to a valve, 28, adapted for directing such recycled retentate back to the second holding vessel, 29. The contents of the first holding vessel, 18, which are concentrated to the desired level are removed from the first holding vessel, 18, via a conduit, 20, and directed by a valve, 21, to a conduit, 39, which connects to a mixing tank, 40, thereby taking the nanofiltration concentrate and introducing it to the mixing tank, 40. The reverse osmosis concentrate which has the desired ethanol level is removed from the second holding vessel, 29, via a conduit, 31, and directed via a valve, 32, to a conduit, 41 which introduces the reverse osmosis concentrate to the mixing tank, 40, wherein it is mixed with the nanofiltration concentrate. A water source, 42, is connected via a conduit, 43, with the second holding vessel, 29, so as to allow introduction of make-up water to the second holding vessel, 29. The product is removed from the mixing tank, 40, by a conduit 44.

Figure 3 relates to a dealcoholization apparatus which comprises a microfiltration membrane module and a reverse osmosis membrane module. Naturally fermented beverage is introduced via a conduit, 11, which has integrated therein a pump, 12, adapted for pressurizing the naturally fermented beverage, into a

microfiltration membrane module, 13, containing a microfiltration membrane, 14. The naturally fermented beverage is passed through the microfiltration membrane, 14, to separate it into a retentate stream containing a high concentration of high molecular weight proteins and betaglycanes which are removed from the microfiltration membrane module, 13, via a conduit, 15. The permeate which has a significantly lower concentration of proteins and betaglycanes is removed from the microfiltration membrane module, 13, via a conduit 16. The flow of permeate from microfiltration membrane module, 13, is controlled by a valve, 28, and such permeate is directed via the valve, 28, to a conduit, 30, which introduces the permeate to a holding vessel, 29. Such liquid is removed from the holding vessel via a conduit, 31, and directed towards a valve, 32, which controls the flow of liquid from holding tank, 29. Such valve, 32, directs the liquid to a conduit, 33, which has integrated therein a pump, 36, which introduces the liquid to a reverse osmosis membrane module, 34, having a reverse osmosis membrane 35. The reverse osmosis membrane module, 34, separates the liquid into a permeate stream comprising a higher concentration of ethanol than the feed stream, which is removed from the reverse osmosis membrane module, 34, via a conduit, 38. The retentate stream, which is lower in ethanol but higher in aroma and flavor containing compounds, is removed from the reverse osmosis membrane module, 34, via a conduit, 37. Such conduit, 37, is connected with a valve, 28, which directs such recycled retentate back to the holding tank, 29. Make-up water source 42, is connected via a conduit, 43, to the holding vessel, 29, such make-up source, 42, is adapted for replacing the permeate from the reverse osmosis membrane module with

water. Once the desired level of ethanol has been achieved in the contents of the holding vessel, 29, such contents can be removed via a conduit, 31, and passed through a valve, 32, which directs it towards a conduit, 41, which is a conduit designed and adapted for removing product from the system.

PATENT CLAIMS:

1. A process for the dealcoholization of a naturally fermented beverage comprising:

A. optionally, contacting a microfiltration feedstream comprising a naturally fermented beverage with a microfiltration membrane having a pore size of from 0.1 to 1.0 microns under conditions such that the feedstream is separated into a microfiltration permeate stream which has a lower concentration of high molecular weight turbidity causing compounds, and a microfiltration retentate stream which has a higher concentration of high molecular weight turbidity causing compounds, as compared to the microfiltration feedstream;

B. optionally, contacting a nanofiltration feedstream comprising a naturally fermented beverage or the microfiltration permeate stream with a nanofiltration membrane having a molecular weight cutoff of from 100 to 10,000 under conditions such that the nanofiltration feedstream is separated into a nanofiltration permeate stream which has a lower concentration of aroma and flavor containing compounds, and a nanofiltration retentate stream which has a higher

concentration of aroma and flavor containing compounds, as compared to the nanofiltration feedstream;

C. contacting a reverse osmosis feedstream comprising the microfiltration permeate or the nanofiltration permeate with a reverse osmosis membrane which selectively permeates ethanol and selectively retains aroma and flavor containing compounds having a molecular weight cut off of from 50 to 100 under conditions such that the reverse osmosis feedstream is separated into a reverse osmosis permeate stream which is higher in ethanol concentration and lower in aroma and flavor containing compounds, and a retentate stream which is lower in ethanol concentration and higher in aroma and flavor containing compounds, as compared to the reverse osmosis feedstream;

characterized in that, either or both of steps A. or B. must be performed, and if step B is performed the reverse osmosis retentate and the nanofiltration retentate are recombined subsequent to step C.

2. A process according to claim 1 comprising:

A. contacting the microfiltration feedstream comprising a naturally fermented beverage with the microfiltration membrane;

B. contacting the nanofiltration feedstream comprising the microfiltration permeate stream with the nanofiltration membrane;

C. contacting the reverse osmosis feedstream comprising the nanofiltration permeate with a reverse osmosis membrane; and

D. recombining the reverse osmosis retentate and the nanofiltration retentate.

3. A process according to claim 1 comprising:

B. contacting a nanofiltration feedstream comprising a naturally fermented beverage with the nanofiltration membrane;

C. contacting the reverse osmosis feedstream comprising the nanofiltration permeate with a reverse osmosis membrane and

D. recombining the reverse osmosis retentate and the nanofiltration retentate.

4. A process according to claim 1 comprising:

A. contacting the microfiltration feedstream comprising a naturally fermented beverage with the microfiltration membrane; and

C. contacting the reverse osmosis feedstream comprising the microfiltration permeate with a reverse osmosis membrane.

5. A process according to Claims 2 or 3 wherein the nanofiltration retentate is recycled and further contacted with the nanofiltration membrane so as to further concentrate the nanofiltration retentate.

6. A process according to one of Claims 1 to 5 wherein the reverse osmosis retentate is recycled and further contacted with the reverse osmosis membrane so as to remove additional ethanol from the reverse osmosis retentate.

7. An apparatus adapted for removing alcohol from naturally fermented beverages which comprises:

A. optionally, one or more microfiltration membrane modules, wherein the microfiltration membrane has a pore size of 0.1 to 1.0;

B. optionally, a means for introducing a naturally fermented beverage to the microfiltration membrane module;

C. optionally, a means for removing a microfiltration retentate from the vicinity of the microfiltration membrane module;

D. optionally, a means for removing a microfiltration permeate from the vicinity of the microfiltration membrane module;

E. optionally, one or more nanofiltration membrane modules, wherein the nanofiltration membrane has a molecular weight cutoff of from 1,000 to 15,000;

F. optionally, a means for introducing a naturally fermented beverage or microfiltration permeate to the nanofiltration membrane module;

G. optionally, a means for removing a nanofiltration retentate from the vicinity of the nanofiltration membrane module;

H. optionally, a means for removing a nanofiltration permeate from the vicinity of the nanofiltration membrane module;

I. one or more reverse osmosis membrane modules, containing a membrane which is capable of

selectively permeating ethanol and selectively retaining flavor and aroma compounds of naturally fermented beverages having a molecular weight cutoff of 50 to 100;

J. a means for introducing microfiltration permeate or nanofiltration permeate to the reverse osmosis membrane modules;

K. a means for removing a reverse osmosis retentate from the vicinity of the reverse osmosis membrane modules;

L. a means for removing a reverse osmosis permeate from the vicinity of the reverse osmosis membrane modules;

characterized in that all of elements A B C and D, if present, are present together, all of elements E F G and H, if present, are present together, and that either the set of elements A B C and D, the set of elements E F G and H, or both sets of elements, must be present;

further characterized in that where elements E F G and H are present the element M shall be included which comprises,

M. a means for combining the nanofiltration retentate and the reverse osmosis retentate.

8. The apparatus according to claim 7 which further comprises:

N. a holding vessel adapted for receiving the nanofiltration permeate from H, the means for removing a nanofiltration permeate from the vicinity of the nanofiltration membrane module, or the microfiltration permeate from the D, a means for removing a microfiltration

permeate from the vicinity of the microfiltration membrane module;

O. a means for transporting the contents of the holding vessel to the reverse osmosis membrane module;

P. a means for recycling the reverse osmosis retentate to the holding vessel; and

Q. a means for adding water to the holding vessel N, to make up for all or part of the volume of reverse osmosis permeate.

9. An apparatus according to Claim 7 or 8 which further comprises:

R. a second holding vessel adapted to hold the material to be fed to the nanofiltration membrane module which comprises a naturally fermented beverage or the permeate from the microfiltration membrane module;

S. a means for recycling the nanofiltration retentate to the second holding vessel R.;

T. a means for transporting the contents of the second holding vessel, R, to the nanofiltration membrane module; and

U. a means of transporting the concentrated retentate contained in the second holding vessel, R, to the a means for combining the nanofiltration retentate and the reverse osmosis retentate M.

Figure 1

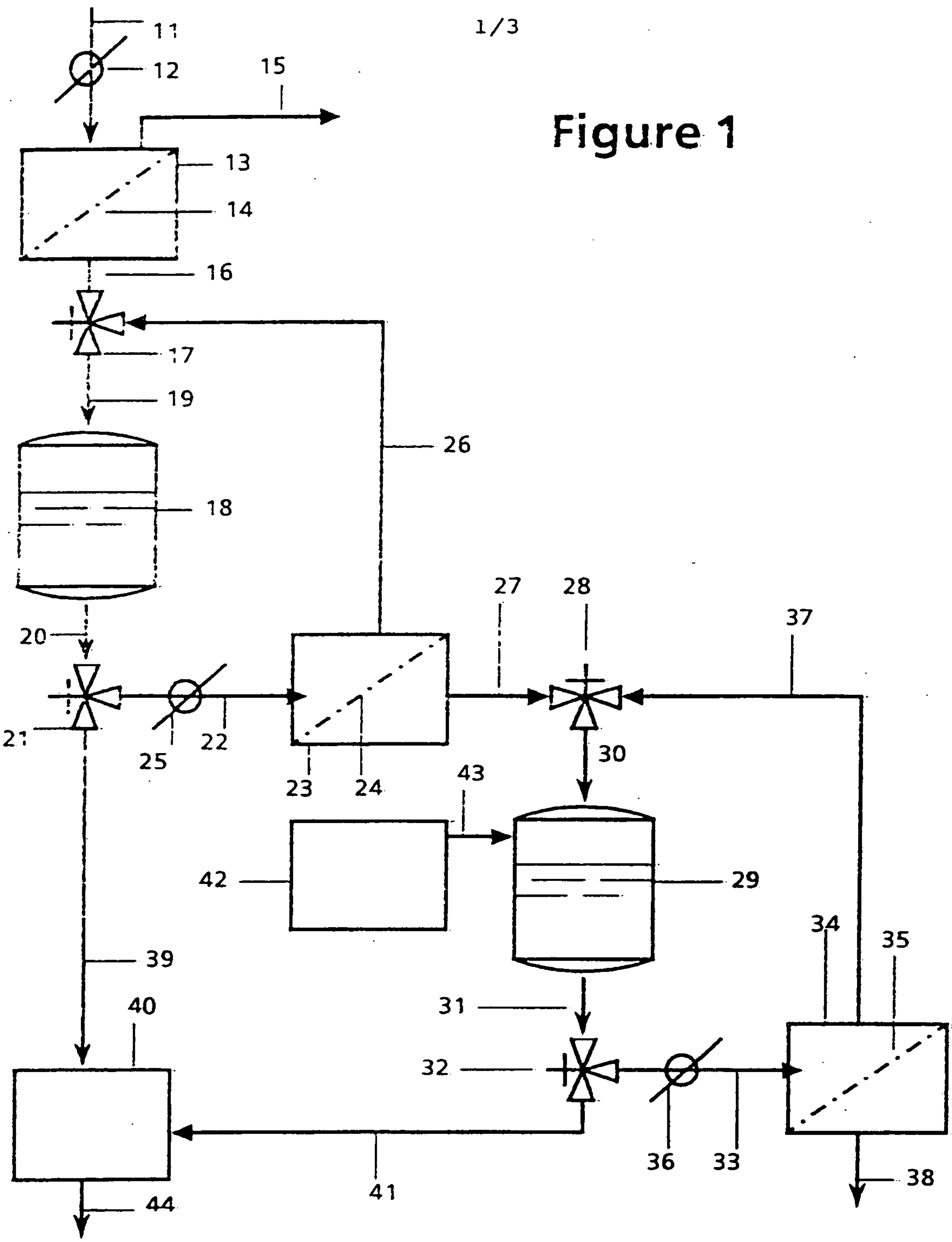

11
12
15
13
14
16
17
19
26
18
20
21
25
22
23
24
27
28
37
30
43
42
29
34
35
39
40
31
32
36
33
38
41
44

Figure 2

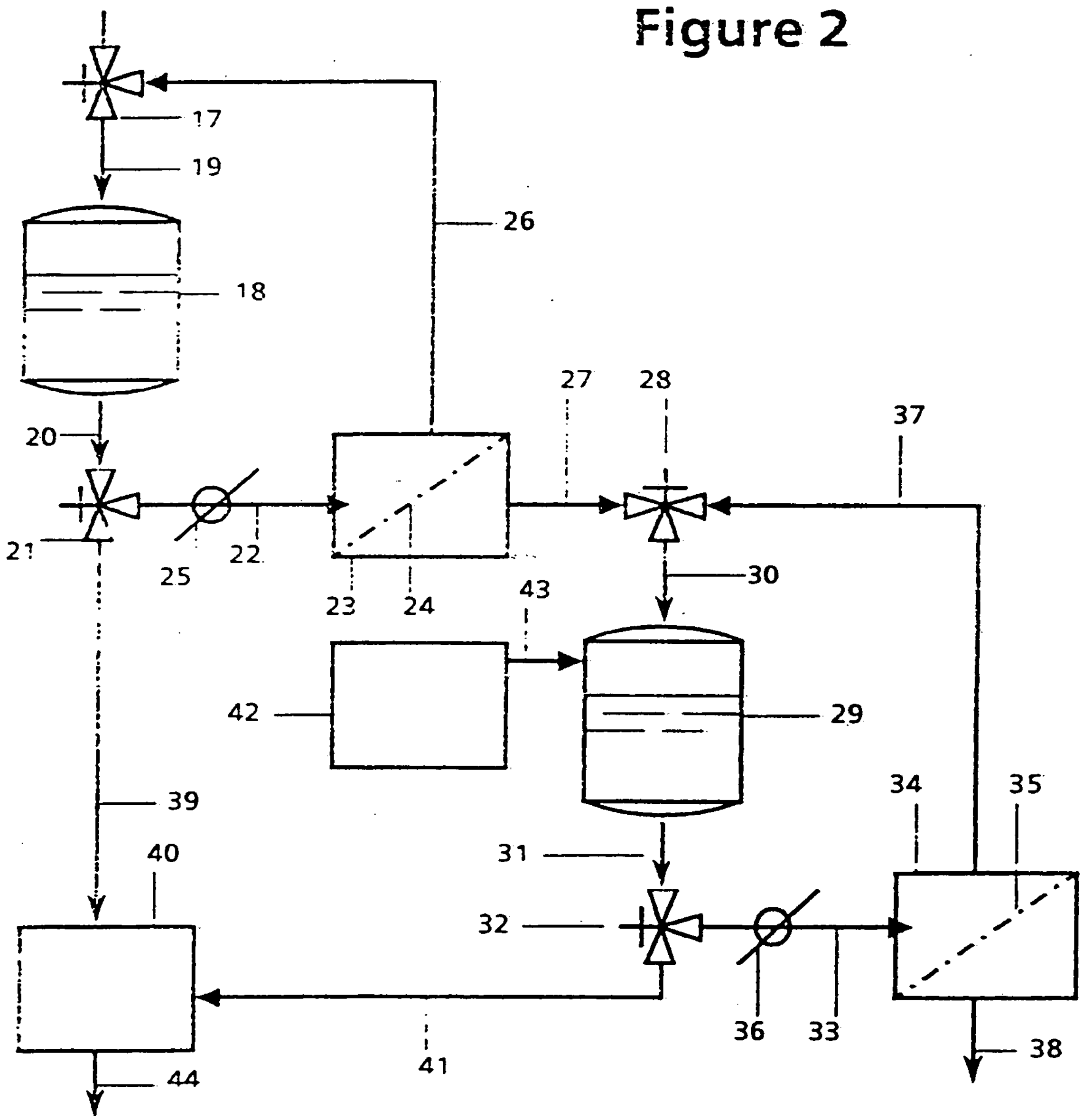
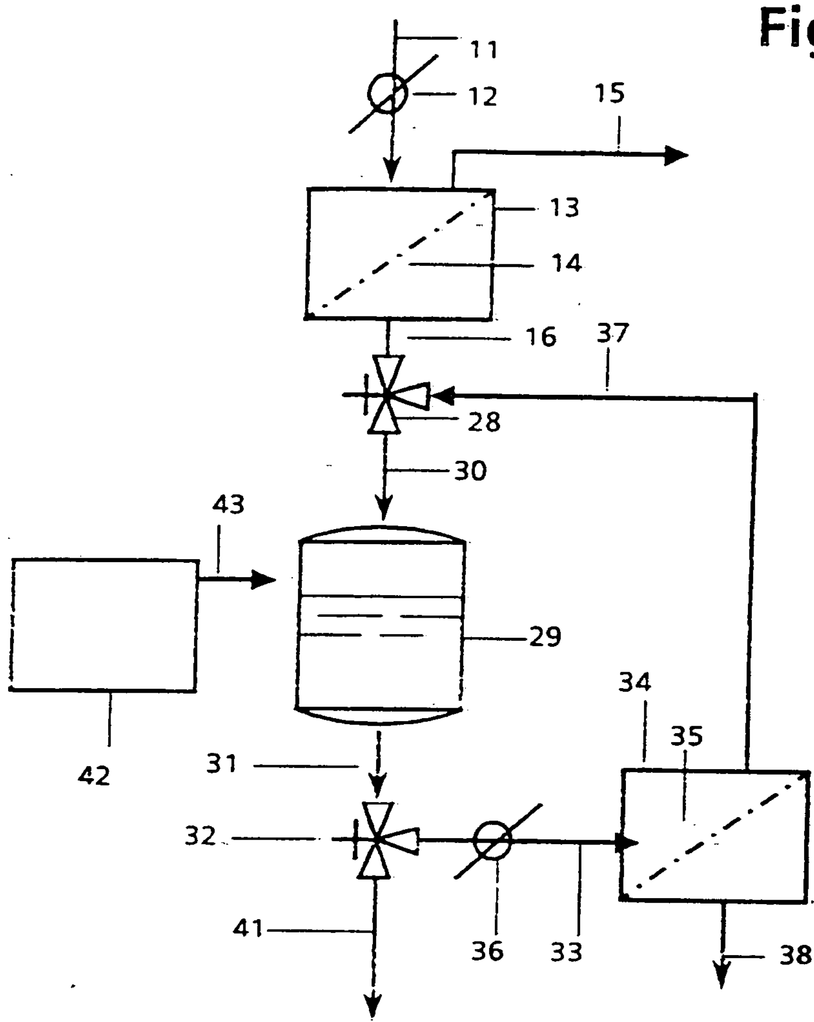

17
19
26
18
27
28
37
20
21
25
22
23
24
30
43
42
29
39
34
35
40
31
32
36
33
38
41
44

Figure 3



INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 91/02120

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C12G3/08

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C12G

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category°	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
Y	EP,A,0 089 893 (UNION DE BRASSERIES) 28 September 1983 see claims ---	1-3,7
Y	WO,A,8 202 405 (M. BONNEAU) 22 July 1982 cited in the application see claims ---	1-3,7
A	DE,A,3 819 139 (APV ROSISTA GMBH) 7 December 1989 see column 2, line 45 - line 63; claims ---	1-2,4-9
A	PATENT ABSTRACTS OF JAPAN vol. 13, no. 273 (C-609)(3621) 22 June 1989 & JP,A,1 067 173 (SAN EI CHEM. IND. LTD.) 13 March 1989 see abstract ---	1,7

° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
28 JANUARY 1992	20. 02. 92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	BEVAN S.R. S Bevan

1

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. EP 9102120
SA 52754

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 28/01/92
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0089893	28-09-83	FR-A-	2524000	30-09-83
		AU-B-	553655	24-07-86
		AU-A-	1263983	29-09-83
		CA-A-	1201398	04-03-86
		JP-A-	58209975	07-12-83
		OA-A-	7353	31-08-84
		US-A-	4532140	30-07-85
WO-A-8202405	22-07-82	FR-A-	2497825	16-07-82
		AU-A-	8000782	02-08-82
		EP-A,B	0069137	12-01-83
		US-A-	4499117	12-02-85
DE-A-3819139	07-12-89	None		

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82